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(54) **High energy and high power lithium batteries, and method for producing the same.**

(57) High energy and high power lithium storage batteries, comprising and anode of lithium or lithium alloy, a non-aqueous electrolytic solution containing a lithium salt in one or more organic solvents or a solid electrolyte consisting of a lithium salt/polymeric material complex, and a cathode based on a lithium-vanadium oxide of nominal stoichiometric formula LiV_3O_8, which is obtained in the amorphous form by means of a new process of synthesis in aqueous solution. The choice of the amorphous form for the cathode material provides better performance with respect to the corresponding material in the crystalline form.

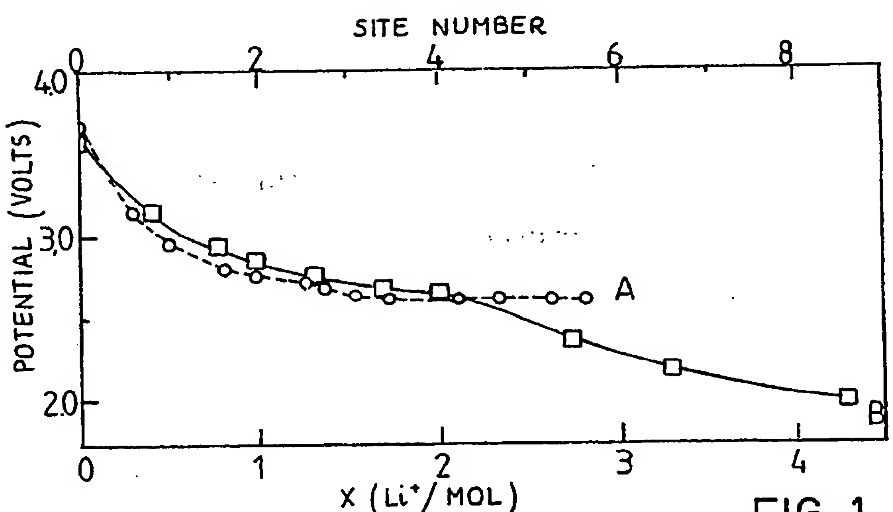


FIG. 1

EP 0 397 608 A2

HIGH ENERGY AND HIGH POWER LITHIUM STORAGE BATTERIES, AND METHOD FOR PRODUCING THE SAME

The present invention relates to high energy and high power lithium batteries as well as to the method for producing the same. More particularly, this invention relates to a lithium secondary cell employing as the cathodic material a lithium-vanadium oxide of such morphology as to show improved properties with respect to the already known materials; the cathodic material is obtained through a specifically conceived procedure.

Lithium anode rechargeable batteries have been available on the market for some years. The batteries based on the Li/MoS_2 pair, produced by Moli Energy (Canada), are the first developed. They are capable of resisting several hundreds of charge/discharge cycles, but their theoretical specific energy (233 Wh/kg, corresponding to 0.8 Li^+/molecule) is not enough for a number of applications.

In recent times, the commercial availability has been announced of storage batteries working on other systems, in particular on $Li/NbSe_3$ and on Li/MnO_2. The theoretical specific energy values of the above-mentioned systems, hovewer, are not particularly high (436 Wh/kg for the first couple, and 415 Wh/kg for the second one).

As is well known in the field, in order to work satisfactorily as a cathode, a material must be such as to supply a high specific capacity and a high energy density, both of which are requisites of fundamental importance. It is also known that other properties are equally important, i.e. a good chemical and electrochemical stability against the organic solutions employed for the electrolyte, as well as the capability of resisting high current levels and long cycling operations, and of enduring overcharging and overdischarging. More over, said material should also be of limited cost and non toxic.

Keeping into account all such requisites, the author of the present invention has already determined a particularly promising cathode material, i.e. a lithium-vanadium oxide of formula $Li_{1+x}V_3O_8$ in crystalline form (monoclinic system), which is the subject-matter of the Italian patent no. 1,148,606.

With the purpose of improving the performance of the lithium-vanadium oxide based cathode, the possibility has been investigated thereafter of modifying the crystalline structure of LiV_3O_8 in order to make the Li^+ ion intercalation easier. It has been found that a positive result could be obtained by applying measures capable of giving rise to an increase in the interlayer distance in the crystalline structure. Particularly effective were the substitution of a part of the Li^+ ions of the compound by Na^+ ions (cathode materials of the formula $Li_{1+x-y}Na_yV_3O_8$ and the intercalation of water molecules into the crystalline lattice. All the above is the subject-matter of the Italian patent application no. 48218 A/88.

Both $Li_{1+x}V_3O_8$ and $Li_{1+x-y}Na_yV_3O_8$ are obtained by high temperature melting (at least 600°C) of V_2O_5 with Li_2CO_3, or with Li_2CO_3 and Na_2CO_3 in the suitable proportions. The melt, once cooled, gives rise to a very solid material which is then to be crushed and milled in order to obtain the cathode material. The process according to the above-mentioned patent application provides, as already pointed out, a cathode material with improved properties with respect to those of the original LiV_3O_8, and comprises, in addition to the above-mentioned procedures, a pressing operation performed at a high pressure. The pressing gives rise to the formation of particles having grain size much smaller than those usually employed.

According to the process od the above-mentioned patent application, in order to obtain a satisfactory mixing with the conductive and binding additives normally used in the cathode mixture, the crystalline oxide in the form of a very fine powder, is suspended together with the additives in methanol and subjected to high speed stirring. Then the methanol is evaporated off and the resulting solid material is milled under dry conditions. After pressing the powder on a nickel grid, the cathode is preferably subjected to sintering.

It can be clearly seen from the above that the appreciable improvement in the properties of the above-mentioned cathode material with respect to the lithium-vanadium oxide of the original patent is counter-balanced by a certain complexity of the production process.

Accordingly, the object of the present invention consists in providing a cathode material of the same kind as those disclosed above, with improved properties as regards its performance in the storage battery, and which is also obtainable by means of a simple and economic process.

Since it has been observed in the previous investigations that a cathode material with particles of the order of some microns shows surely better performance than a material with 20-30 μm granulometry, the synthesis has been considered of a compound having the same chemical formula as the preceding materials but with a still more favourable morphology.

This can be obtained if the lithium-vanadium oxide is in the amorphous form instead of being in the crystalline form, and such amorphous form can

be obtained through a specifically devised process, which has in addition the advantage of being extremely simple when compared to the synthesis performed by high temperature melting.

It is to be observed that the technical literature in the field reports the possibility of preparing a form of LiV_3O_8 which contains a remarkable percentage of the amorphous compound, and this possibility has been studied by the author of the present invention. The process in question consists in cooling the LiV_3O_8 melt suddenly after bringing the same to 800-900 °C. The material thereby obtained, which is already partially crystalline, loses a remarkable part of its amorphous character when it is finely milled to ensure acceptable electrochemical performance. The need for a high temperature synthesis, as well as for a rapid cooling technique (which usually involves the use of rollers) and for methods capable of giving a finely milled product make the whole process quite complicated. Moreover, the final product, as already remarked above, is again largely crystalline. In view of the foregoing, the said process is not preferable to the process disclosed in the present invention.

According to the present invention, it is suggested to produce LiV_3O_8 in its amorphous form by synthesis in water solution, by reaction between lithium hydroxide, LiOH, and vanadium pentoxide, V_2O_5, in the suitable proportions. The reaction, which can be carried out also at room temperature, gives rise to a precipitate of very fine LiV_3O_8 particles, which showed completely amorphous on X-ray examination.

In order to ascertain that the compound was actually LiV_3O_8, the same was heated up to 350 °C. At that temperature the compound becomes crystalline and accordingly its structure can be compared to that of LiV_3O_8 synthesized at high temperature. The two compounds were shown to be the same on X-ray analysis.

Accordingly, the present invention specifically provides a high energy, high power lithium storage battery comprising a lithium anode or an anode of a lithium alloy with one or more metals, a non-aqueous electrolytic solution containing a lithium salt in one or more organic solvents, or a solid electrolyte made of a lithium salt/polymeric material complex, and a cathode based on a lithium-vanadium oxide of nominal stoichiometric formula LiV_3O_8, which is characterized in that said oxide is in its amorphous form.

As already mentioned above, the amorphous oxide can be obtained from the following reaction carried out in water solution:

$2\ LiOH + 3\ V_2O_5 \rightarrow 2\ LiV_3O_8 + H_2O$

in which the two reactants are to be employed in the $LiOH/V_2O_5$ molar ratio of 2/3.

Such reaction is carried out with stirring at room temperature or, if desired, by moderate heating.

As it is well known, the cathode contains conducting additives such as graphite, acetylene black and carbon, and binding additives, such as Teflon, polyethylene and polypropylene. Due to the extreme fineness of the amorphous oxide particles of the present invention, it may by advantageous to employ the wet mixing technique already disclosed in the above-referred previous patent application, as it will be illustrated in a detailed way below.

The metal alloyed with lithium can be selected from aluminum, cadmium, tin, bismuth, chromium, manganese and lead, while the lithium salt in the electrolytic solution or in the solid electrolyte can be $LiClO_4$, $LiAsF_6$ $LiBF_4$ or $LiCF_3SO_3$.

The organic solvents to be employed in the storage battery of the present invention are preferably propylene carbonate, ethylene carbonate, dimethoxyethane, methylformate, tetrahydrofuran, 2-methyltetrahydrofuran, sulfolane and mixtures thereof.

Polyethylene oxide, polypropylene oxide and mixtures thereof are preferred as polymeric materials for the solid electrolyte.

The production process, which is a further provided by the present invention, comprises, as initial steps, the operation of dissolving the predetermined amount of powder LiOH in water and of adding V_2O_5 progressively till a molar ratio of $LiOH/V_2O_5$ of about 2/3 is reached, while keeping the whole mixture under stirring. The operation is carried out at room temperature, or at a relatively higher temperature if a faster reaction is desired.

It is important that the addition of vanadium pentoxide be completed up to the predetermined molar ratio, as the reaction develops through the formation of intermediate products ($Li_3VO \rightarrow LiVO_3 \rightarrow LiV_3O_8$) which disappear when the correct ratio has been reached.

After keeping the reaction mixture under stirring for a period of time between 24 and 40 hours, preferably for about 24 hours, LiV_3O_8 can be separated in the form of a very fine precipitate. According to the process of the present invention, the product is preferably washed with water once or twice; owing to the slow sedimentation rate, it is convenient to separate the precipitate by centrifugation.

Then the product is dried in oven at 100-200 °C, so that a fine powder of amorphous LiV_3O_8 is obtained.

Thereafter, according to the process of the present invention, LiV_3O_8 is mixed with the conductive and binding additives (in particular acetylene black and Teflon in the weight ratio to one another of 2/1 and in such amount as to form a weight proportion amount of 20-30% of the whole

cathode mixture), by employing the following wet mixing technique: the components are dispersed in a liquid in which they are insoluble, preferably in methanol, then they are mixed by high-speed stirring and thereafter the solvent is evaporated off. The resulting solid, which is made of a very homogeneous mixture of the cathode components, is milled.

The resulting powder is then made compact by pressing it on a nickel grid. It has been also found that it is particularly advantageous to perform a final re-drying treatment of the cathode tablet, preferably at 100-260 °C, more preferably at about 200 °C.

The cathode so obtained, inserted into a battery having a lithium anode and a non-aqueous electrolyte, has shown a clearly better performance than that of the crystalline material, both in single discharge operation and in prolonged cycling.

The results of some experiments carried out with a storage battery manufactured according to the preferred solutions mentioned above, together with their interpretation on a theoretical based are shown in the diagrams of the enclosed drawings, in which:

Figure 1 shows the open-circuit voltage of the cells as a function of the amount of lithium ions inserted into the microstructure during discharge;

Figure 2 shows the voltage specific capacity curves during discharge;

Figure 3 shows the behaviour of the specific capacity at an increasing number of charge and discharge cycles; and

Figure 4 shows the specific capacity as a function of the discharge conditions.

The storage battery according to the present invention to which the following examples refer has a lithium anode supported on Ni, an electrolytic solution consisting of $LiClO_4$ in propylene carbonate dimethoxyethane and a cathode based on amorphous LiV_3O_8, obtained according to the preferred solutions of the above-disclosed process, with the addition of acetylene black/Teflon in the relative ratio of 2/1 and in a total amount of 30% by weight.

The performance of such battery is compared to that of a similar battery having a cathode based on a crystalline LiV_3O_8.

From the curves of Fig. 1 (A for the crystalline oxide and B for the amorphous oxide) it can be observed that the amorphous material allows a higher battery capacity to be obtained. Indeed, in the case of the amorphous material, the value of x in $Li_{1+x}V_3O_8$ during discharge (Li^+ ions being intercalated) can attain a maximum value of about 4.3, whereas for the crystalline oxide the maximum value is slightly less than 3. This means that the amorphous oxide is capable of intercalating a larger amount of Li^+ ions in its unit cell. Actually, the long-range crystallographic order lacks in an amorphous compound, while the short-range order is preserved.

In the amorphous compound, which is endowed with a higher flexibility because of the absence of a long-range order, the unit cell can be modified upon the intercalation of Li^+ ions. This plasticity causes further sites to be created inside the unit cell, in which sites said Li^+ ions can reside: the number of sites that can be occupied ranges from a maximum value of about 6 in the crystalline compound to a maximum of about 9 in the amorphous compound. With an x value of 4.3 and with an average voltage of 2.58 V, both of which being obtainable from Fig. 1 for the amorphous material, it is possible to obtain specific capacity and specific energy values respectively, of 400 Ah/kg and 1,032 Wh/kg. The latter value, if the amount of intercalated lithium is also accounted for (4.3 Li^+/molecule) gives rise to a value of 935 Wh/kg for the Li/LiV_3O_8 pair. Such specific energy is higher than those of the already mentioned materials MoS_2, $NbSe_3$ and MnO_2, and it is also higher than those of other known cathodes such as TiS_2, V_6O_{13}, Li_xCoO_2 and V_2O_5. It is to be observed that the intercalation of Li^+ in the amorphous compound is largely reversible, i.e. almost all lithium intercalated during discharge can be disintercalated in the battery charge.

To such considerations concerning the microstructure of the amorphous material, other considerations are also to be added concerning the macrostructure, which is characterized by the extreme fineness of the particles. Electronic microscope analysis has shown the presence of soft particles of 1 micron size or less, which show a tendency to form incoherent clusters that are easily crushed during the formation of the cathodic mixture. The fineness of the particles is indeed fundamental for a good performance of the cathode itself, above all under severe conditions of charge/discharge.

More particularly, the following advantages can be obtained:

- no breaking of the large particles occurs following to the intercalation/disintercalation cycles, so that no contact losses occur;
- a better contact is obtained between the active material and the conductive additive, so that it is possible to apply very high currents;
- the electrolyte can reach into the innermost layers of the cathode so reducing polarization phenomena.

Such advantages can be put into evidence both in discharge operations and in cycling at high current values. For example, in Fig. 2 the voltage vs. capacity curves are compared for a storage

battery with a crystalline oxide (curve A) and for that of the present invention (curve B) under discharge conditions of 1.5 C (where C is the capacity of the battery), at the tenth discharge cycle. The discharge condition of 1.5 C corresponds to a current of 3.2 mA/cm^2, whereas the charge current was 2.1 mA/cm^2. The storage battery with the amorphous oxide can supply, at a higher voltage, a higher capacity (0.207 Ah/g as opposed to 0.146 Ah/g, down to 1.7 V).

If, in addition, the cycling is considered in its full development, it is also more evident that the amorphous material is superior, as can be seen in the following examples.

EXAMPLE 1

Two cells (B and C) of the button type comprising a Li disc as the anode, an electrolytic solution consisting of $LiClO_4$ in propylene carbonate-dimethoxyethane, a cathode obtained by pressing under 10 t/cm^2 a mixture of amorphous LiV_3O_8 and acetylene black/Teflon (70/30) were subjected to cycles at 1.5 C on discharge and at 1 C on charge. The two cells differed from each other only for the temperature of the final heat treatment, to which the cathode had been subjected, which temperature was of 100°C for cell B, and of 200°C for cell C. A similar cell (A), which contained however a cathode based on a crystalline material, was also tested in a parallel way. In Fig. 3, the curves A, B and C refer to the corresponding cells.

As it can be observed, the storage batteries of the present invention withstand a higher number of cycles and have higher capacities with respect to the crystalline compound. Moreover, it can be remarked that the cathode which has undergone a re-drying at 200°C shows a better behaviour than the one re-dried at 100°C; such behaviour is attributed supposedly to a more complete removal of the water incorporated in the oxide during the synthesis in aqueous solution. Additionally, also a normal heat treatment at 100°C gives a cathode of performance remarkably better than a cathode based on a crystalline oxide.

EXAMPLE 2

Two cells produced according to example 1, one of them containing the cathode based on the amorphous material, re-dried at 200°C, and the other containing the crystalline material, were subjected to cycling under high conditions (from 1.5 C to 4 C on discharge, while the charge was always at C). Fig. 4 shows clearly that the amorphous material (curve B) gives rise to specific capacities remarkably superior to those of the crystalline compound (curve A) under all conditions.

The present invention has been disclosed with particular reference to some preferred embodiments thereof, but it is to be understood that modifications and changes can be brought to it without departing from its true spirit and scope.

Claims

1. A high energy, high power lithium storage battery comprising an anode of lithium or of a lithium alloy with one or more metals, a non-aqueous electrolytic solution containing a lithium salt in one or more organic solvents, or a solid electrolyte consisting of a lithium salt/polymeric material complex, and a cathode based on a lithium-vanadium oxide corresponding to the nominal stoichiometric formula LiV_3O_8, characterized in that said oxide is in its amorphous form.

2. A storage battery according to claim 1, wherein the said amorphous oxide is obtainable by reaction of LiOH with V_2O_5 in the molar ratio of about 2/3 in aqueous solution.

3. A storage battery according to claim 2, wherein the said reaction in aqueous solution is carried out at room temperature.

4. A storage battery according to each one of the preceding claims 1-3, wherein the said cathode also contains conductive additives such as graphite, acetylene black and carbon.

5. A storage battery according to each one of the preceding claims 1-4, wherein the said cathode also contains binding additives, such as Teflon, polyethylene and polypropylene.

6. A storage battery according to each one of the preceding claims 1-5, wherein the said metal alloyed with lithium is selected from the group consisting of aluminum, cadmium, tin, lead, bismuth, chromium and manganese.

7. A storage battery according to each one of the preceding claims 1-6, wherein the said lithium salt is selected from the group consisting of $LiClO_4$, $LiAsF_6$, $LiBF_4$ and $LiCF_3SO_3$.

8. A storage battery according to each one of the preceding claims 1-7, wherein said one or more organic solvents are selected from the group consisting of: propylene carbonate, ethylene carbonate, dimethoxyethane, methylformate, tetrahydrofuran, 2-methyltetrahydrofuran, sulfolane and mixtures thereof.

9. A storage battery according to each one of the preceding claims 1-7, wherein the said polymeric material in the solid electrolyte is selected

from the group consisting of polyethylene oxide, polypropylene oxide and mixtures thereof.

10. A process for the production of a lithium storage battery according to claims 1-5, wherein the preparation of the cathode comprises the following steps:

a) dissolving powder LiOH into water

b) adding V_2O_5 progressively and under stirring up to a molar ratio $LiOH/V_2O_5$ of about 2/3

c) separating, after about 24-40 hours from the start of the reaction, the precipitate so obtained, washing it with water and then separating it from the water

d) drying the product of the preceding step so as to obtain a fine LiV_3O_8 powder

e) mixing the said powder oxide with the cathodic additives, by dispersing the said materials in a solvent in which they are insoluble, then stirring at high speed and then evaporating the solvent off

f) milling the solid product obtained from the preceding step

g) pressing said product on a nickel grid

h) re-drying the cathode tablet by heating.

11. A process according to claim 10, wherein the said separation of the precipitate obtained as the product in step c) is carried out 24 hours after the start of the reaction.

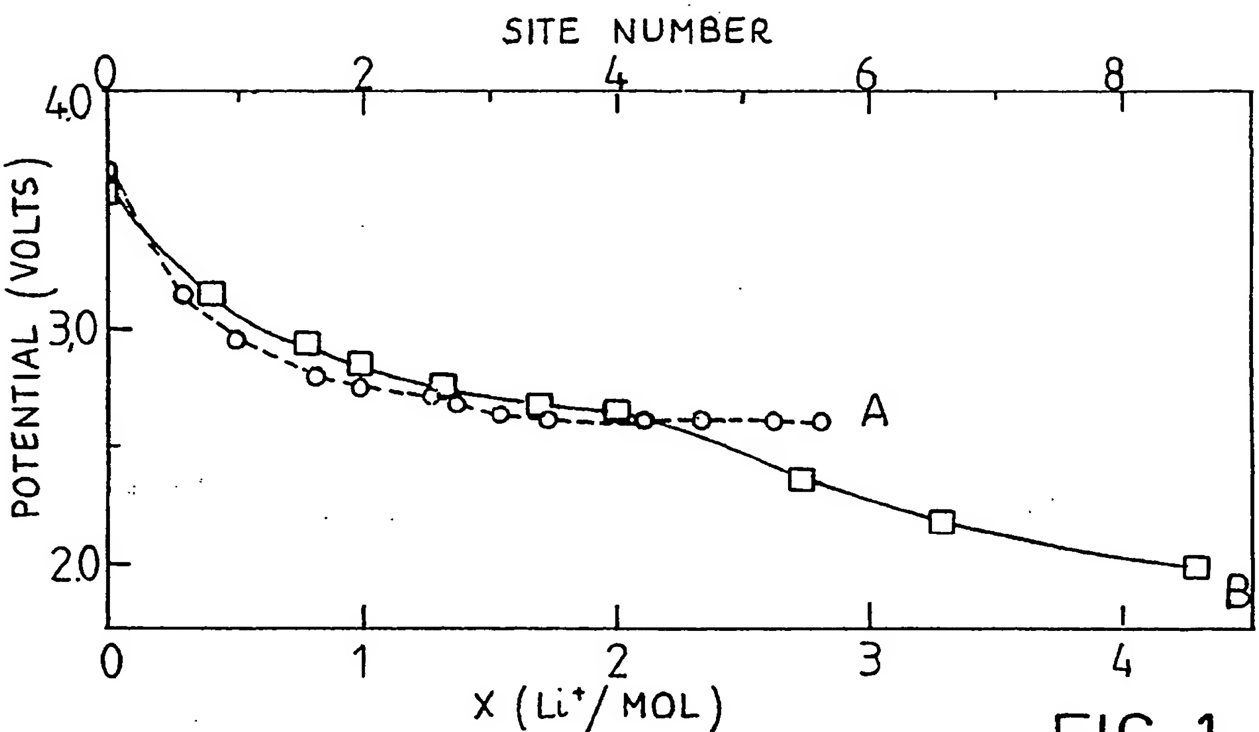
12. A storage according to claim 11, wherein the said reaction is carried out at room temperature.

13. A process according to each one of the preceding claims 10-12, wherein the said drying step d) is carried out in oven at 100-200 °C.

14. A process according to each one of the preceding claims 10-13, wherein the said cathode additives are acetylene black and Teflon in the weight ratio of 2/1 with respect to one another, and they are added in such amount as to form a weight proportion of 20-30% of the cathode mixture.

15. A process according to each one of the preceding claims 10-14, wherein the said final redrying is carried out at a temperature between 100 and 260 °C.

16. A high energy, high power lithium storage battery and the method for the production of the same, according to claims 1-15, substantially as disclosed and illustrated above.


SITE NUMBER
0
2
4
6
8
4.0
3.0
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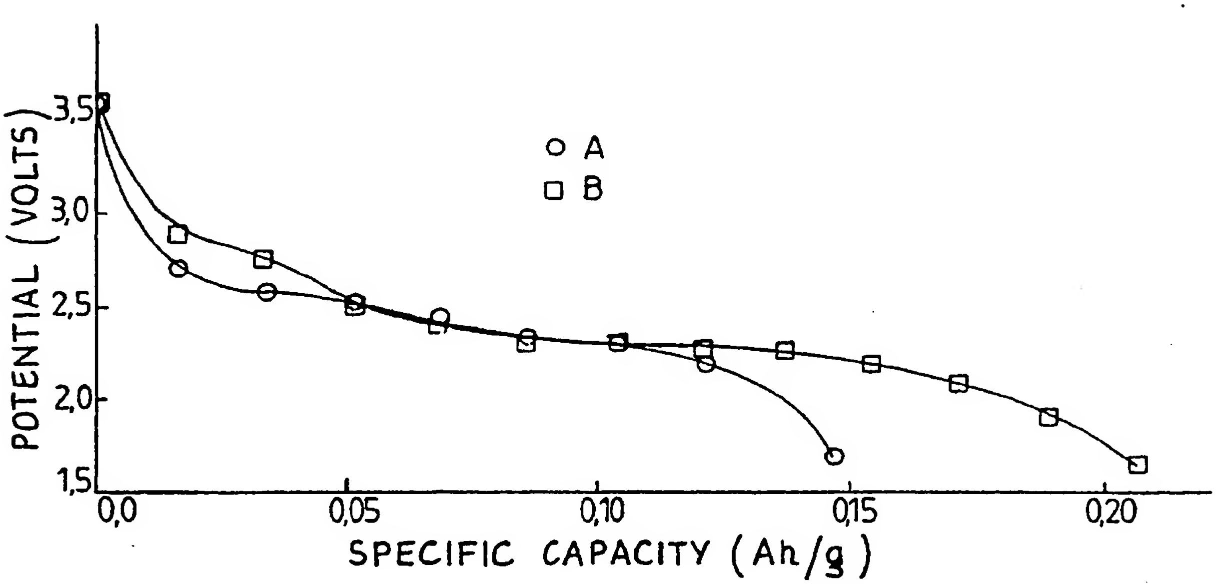
POTENTIAL (VOLTS)
A
B
0
1
2
3
4
X (Li+/MOL)

FIG. 1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□ B
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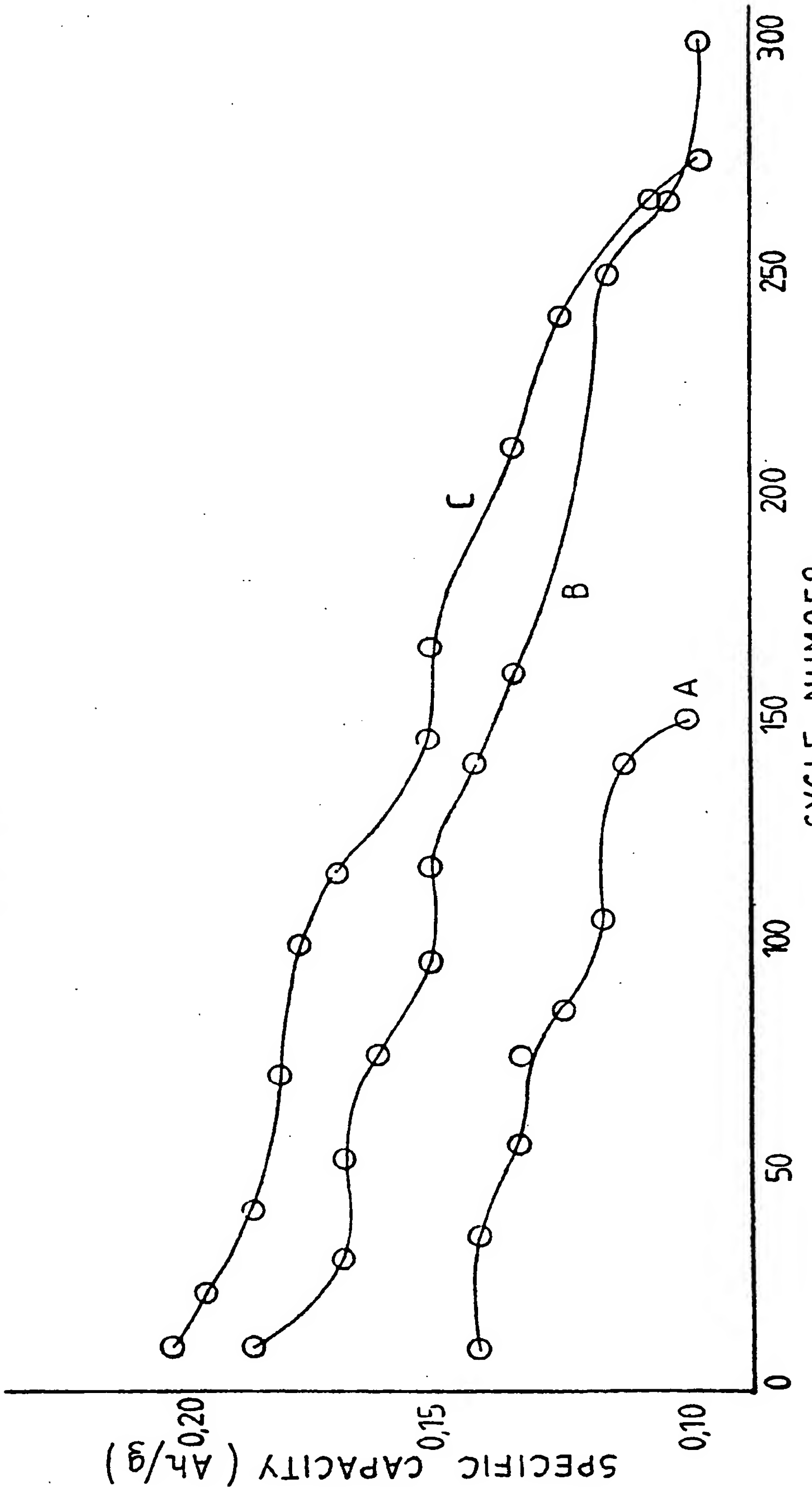
SPECIFIC CAPACITY (Ah/g)

FIG. 2

FIG. 3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0,10
CYCLE NUMBER
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150
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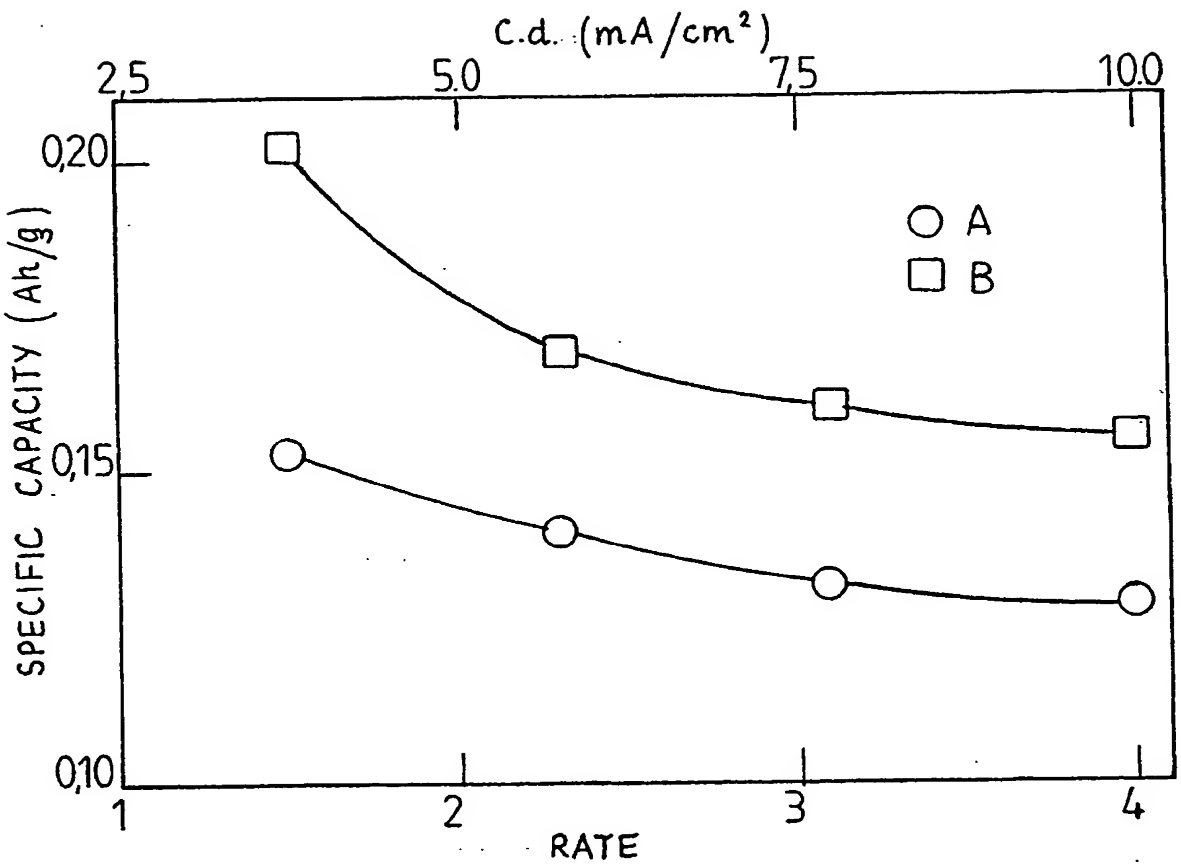
250
300
A
B
C


C.d. (mA/cm²)
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7,5
10.0
0,20
0,15
0,10
SPECIFIC CAPACITY (Ah/g)
A
B
1
2
3
4
RATE

FIG. 4

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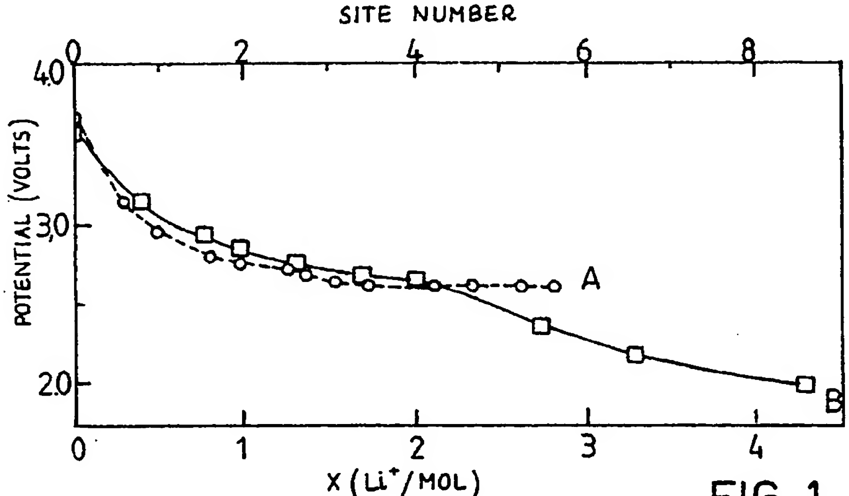

FIG. 1

EP 0 397 608 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 83 0142

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 133, no. 12, December 1986, pages 2454-2458, Manchester, NH, US; M. PASQUALI et al.: "Li/Li1 + xV3O8 batteries" * Page 2455, left-hand column, paragraphs 2,4-5,8-11; page 2456, table 1; page 2456; page 2457, left-hand column, paragraph 3 *	1,4,5,7,8, 16	H 01 M 4/48 H 01 M 4/58 H 01 M 10/40 C 01 G 31/00
Y	IDEM	6	
A	IDEM	14	
X	CHEMICAL ABSTRACTS, vol. 95, no. 10, 1981, page 471, abstract no. 88083z, Columbus, Ohio, US; K. NASSAU et al.: "The quenching and electrochemical behavior of lithium oxide-vanadium pentoxide glasses", & J. NON-CRYST. SOLIDS 1981, 44(2-3), 297-304 * Abstract *	1,8,16	
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Y	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 130, no. 5, May 1983, pages 1225-1227, US; S. PANERO et al.: "Rechargeable Li/Li1 + xV3O8 cells" * Page 1225, right-hand column, paragraph 2 *	1,9	H 01 M C 01 G
Y	JOURNAL OF APPLIED ELECTROCHEMISTRY, vol. 18, 1988, pages 401-404, Chapman and Hall Ltd; F. CROCE et al.: "Characteristics of a poly(ethylene oxide)-LiBF4 polymer electrolyte" * Page 404, left-hand column, paragraph 3; page 404, right-hand column, lines 33-34 (reference 14) *	1,9	

-/-

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	22 November 90	D'HONDT J.W.

CATEGORY OF CITED DOCUMENTS

- X: particularly relevant if taken alone
- Y: particularly relevant if combined with another document of the same catagory
- A: technological background
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- D: document cited in the application
- L: document cited for other reasons
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A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 135, no. 1, January 1988, pages 12-15, Manchester, NH, US; F. BONINO et al.: "A polymeric electrolyte rechargeable lithium battery" * Page 12, left-hand column, lines 20-24; abstract; page 15, right-hand column, lines 45-46 (reference 9) *	9	
A	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 110 (E-496)[2557], 7th April 1987; & JP-A-61 259 455 (SHOWA DENKO K.K.) 17-11-1986 * Abstract *	1,7,8,16	
A	FR-A-2 616 013 (ETAT FRANCAIS)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

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A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document